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Nuclear Sciences and Technology Services

Minimisation of Uranium Corrosion When Treating Hanford KE and KW Basin Wastes Using Cementation

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Nuclear Sciences and Technology Services

Minimisation of Uranium Corrosion When Treating Hanford KE and KW Basin Wastes Using Cementation

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22nd April 2004

Checked by :

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Hanford, uranium, corrosion, cementation, K-Basin, KE, KW, WIPP, Central Waste Complex, modelling, shielding, process viability, encapsulation, BFS, OPC

EXECUTIVE SUMMARY

The work reported in NSTS (04) 4992[1] concluded that the uranium corrosion rates observed in a high water content BFS/OPC matrix are similar to those observed in water and as such a high water content BFS/OPC matrix is likely to be the optimum matrix for achieving corrosion of the uranium from KE and KW basin wastes during storage before transport. The trials in this report are intended to optimise the grout formulation to minimise the corrosion rate of encapsulated uranium during storage and transport.

Ten uranium corrosion trials using stainless steel reactor vessels, and having a nominal volume of 25 litres have been used to investigate the corrosion rate of uranium metal by measuring the pressure increase in a sealed system due to the hydrogen evolved from the corrosion reaction.

Each reactor vessel was charged with a known surface area of metal which was generated by using 30 natural uranium 'pennies'. Each trial was conducted at a nominal constant curing temperature of 60°C to replicate the temperature during transport. Grout was prepared to replicate the composition of the grout following encapsulation of KE and KW wastes and the following methods of reducing the corrosion rate were investigated:

- Reducing the water content of the encapsulating grout.
- Using a grout which does not react with any oxygen present.
- Producing a grout which allows oxygen ingress.
- Including an additive that generates oxygen.

It was found that

- Increasing the total solids content and reducing the water content of the grout has reduced the corrosion rate of uranium to a factor of about 0.4 at 55 to 65°C. Data is required to confirm this reduction is still applicable at lower temperatures.

- Modelling studies of the hydrogen generation from encapsulated KE and KW wastes should use the following expression to model scenarios where a formulation is selected to maximise the uranium corrosion rate:

$$\text{Ln rate} = \frac{-9298.1}{\text{Temperature (K)}} + 32.008 \qquad \text{g/m}^2\text{/day} \quad (3)$$

- Where the scenario being modelled uses a grout selected to minimise corrosion this expression should be used for the uranium corrosion rate:

$$\text{Ln rate} = \frac{-8679.9}{\text{Temperature (K)}} + 29.227 \qquad \text{g/m}^2\text{/day} \quad (4)$$

- The maximum rate is likely to be less than twice and the minimum is likely to be about 0.2 of that in equation 3. These ratios should be applied to the corrosion rates predicted by equation 3 to assess the sensitivity of the model to the variability in corrosion rate.

- Monitoring of the samples should be continued at least until hydration is complete to measure any further reduction in rate caused by this hydration. During this continued monitoring the curing temperature should be reduced at a suitable time to generate corrosion rate data at lower temperatures.

VERIFICATION STATEMENT

This document has been verified and is fit for purpose. An auditable record has been made of the verification process. The scope of the verification was to confirm that:

- The scope is accurate and represents the customer requirements
- The constraints are valid
- The assumptions are reasonable
- The document demonstrates that the project is using the latest company approved data
- The document is internally self consistent

HISTORY SHEET

Issue Number	Date	Comments
Issue 1	23/4/04	Issued to BNFL Inc and Fluor Hanford
Issue 2	07/06/04	Responses to customer comments added

This copy number

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1. Introduction

The K-basins (KE and KW) located on the Hanford site in Washington State, were constructed in the 1950's to receive spent nuclear fuel from the Hanford 100 K East (KE) and 100 K West (KW) reactors, which operated from 1955 to 1970 and 1971 respectively. Subsequently both KE and KW basins were upgraded and operated from the mid 1970's for the storage of N reactor fuel, the principal difference in the operating regime being that KE utilised fuel storage in open canisters, with KW using closed canisters.

Since 1994 US Department of Energy (DOE) and its contractors have been engaged in a project to remove the approximately 2,100 metric tons of spent fuel from the K-basins and transport the material to an interim dry storage facility located in another area of the Hanford site.

The material remaining in the K-Basins consists of approximately 50m^3 of contaminated sludge which now requires treatment and packaging in order to allow the decommissioning of the K-basins. The sludge is a unique, non-homogeneous mixture possibly containing corroded fuel (i.e. uranium oxides, hydrates, hydride), cladding pieces, debris such as windblown sand and insects, rack and canister corrosion products, ion exchange resin beads, polychlorinated biphenyls, and/or fission products. The total volume of the material is approximately 50m^3 (KE being approximately 42 m^3 and KW being approximately 8m^3) with the particle size of the solid material being less than ¼ inch (6.35mm).

The timescales to develop a treatment method for the K-basin sludge is that all of the sludge should be treated, packaged and sent for interim storage at the Central Waste Complex (CWC) by the end of August 2007. Final disposal will be at the Waste Isolation Pilot Plant (WIPP) as RH-TRU.

There are two options for sludge treatment – blend all the waste streams into one (recognizing that it will not in reality be homogeneous) or treat KE and KW separately. There is a strong driver to treat the sludge separately and start packaging of KE sludge as early as possible, hence the streams to be considered for this study are:

1) KE blend
2) KW
    a. floor/pit & settler
    b. NLOP (North Load Out Pit)
    c. KOP (Knock Out Pot)
3) KE blend + KW KOP
4) KW blend (excluding KOP)

The principal requirements for the final product from any packaging process are that there should be no free liquid and it shall not produce sufficient hydrogen gas during transport to WIPP to create a flammable environment within the cask. There is no requirement for the product to meet any other physical or chemical criteria.

In order to meet the requirements of the safety case for the transport of the treated waste to WIPP, a modelling assessment is required to confirm that not more than 5 volume % hydrogen will be generated in the ullage spaces of the waste container and the RH-72B transport container. The maximum time over which transport may occur is 60 days, at a maximum temperature of 60°C.

As a result of initial discussions between BNFL Nuclear Sciences and Technology Services (NSTS), BNFL Inc., Fluor-Hanford (FH) and Pacific Northwest National Laboratory (PNNL) in January 2004 a contract was awarded to BNFL NSTS to perform an initial assessment of the viability of the use of cementation for the packaging of the K-basin sludges in terms of:

- the engineering viability of the process to treat the waste
- the number of drums of treated waste which will be generated within the constraints of the transport safety case.

The overall scope of this assessment is defined in the proposal document (CEM-P-2004-01) and can be summarised as:

1. Through a review of sampling data and simulant testing, define and optimise a reference grout formulation, in terms of the uranium corrosion which is a key driver for the transport of the treated material to WIPP.
2. Model the system to assess the effects of waste loading, particle size, Particle Size Distribution (PSD), temperature, time and ullage volume, vent size and type on the ability of waste packages to meet the 5 vol% hydrogen limit for the WIPP safety case. This modelling will utilise the existing data which NSTS has generated on the corrosion of uranium metal in cement systems along with additional corrosion data generated in the project.
3. Assess viability of mobile grout process and define conceptual process flowsheet
4. Produce preliminary dose shielding (n, β, γ) assessment to determine contact dose on outside of waste drum.
5. Produce a report of work conducted and present information to Fluor Hanford by 30th April 2004.

The Encapsulation Team within the Nuclear Sciences and Technology Services (NSTS) group of BNFL have been investigating the corrosion behaviour of uranium metal encapsulated in a blast furnace slag and ordinary Portland cement matrix for several internal BNFL projects. This work is reported in NSTS (04) 4992[1] which concluded that the rates observed in a BFS/OPC matrix are similar to those observed in water and as such a BFS/OPC matrix is likely to be the optimum matrix for achieving corrosion of the uranium during storage before transport. This high corrosion rate could be used to ensure that sufficient uranium has been corroded in this storage period so that when the waste is transported there is little uranium left for corrosion. The alternative is that the hydrogen generation rate is minimised and hence waste loadings per drum can be optimised.

The trials in this report are intended to optimise the grout formulation to minimise the corrosion rate of encapsulated uranium. This will optimise waste loadings per drum by reducing the uranium corrosion rate in the short and long term so that the rate of hydrogen

generation is minimised. A number of potentially optimised grout formulations have been selected based on a knowledge of cement chemistry[1], uranium corrosion mechanisms[1] and small scale trials with an inactive simulant[2]. The options investigated were:

- Reducing the water content of the encapsulating grout.
- Using a grout which does not react with any oxygen present.
- Producing a grout which allows oxygen ingress.
- Including an additive that generates oxygen.

2. Scope

Ten uranium corrosion trials using stainless steel reactor vessels, and having a nominal volume of 25 litres have been used to investigate the corrosion rate of uranium metal by measuring the pressure increase in a sealed system due to the hydrogen evolved from the corrosion reaction.

Each reactor vessel was charged with a known surface area of metal which was generated by using 30 natural uranium 'pennies' nominally measuring 28 mm diameter by ~10 mm thick. Each trial was conducted at a nominal constant curing temperature of 60°C to replicate the temperature during transport. Grout was prepared to replicate the composition of the grout following encapsulation of KE and KW wastes and the following grout formulations were investigated:

1. KW Basin North Load Out Pit simulant 75:25 PFA/OPC Superplasticiser
2. KW floor / pit & settler in 75:25 PFA/OPC Superplasticiser
3. KW KOP 75:25 PFA/OPC Superplasticiser
4. KE Blend 75:25 PFA/OPC Superplasticiser
5. KE Blend 80:20 BFS/OPC Superplasticiser
6. KE Blend 100% OPC Superplasticiser & Cenospheres
7. KE Blend 75:25 PFA/OPC Superplasticiser & Barium Peroxide
8. KE Blend 75:25 PFA/OPC Superplasticiser
9. KE Blend 100% OPC Superplasticiser
10. KE Blend 80:20 BFS/OPC No additives

The corrosion rate of uranium was then determined by measuring the change in pressure caused by hydrogen evolution via pressure transducers in the stainless steel reaction vessel lid.

3. Experimental procedure

The Encapsulation Team within NSTS have over 20 years experience of generating and analysing data to understand the corrosion of reactive metals such as aluminium, Magnox, and uranium in cement and other matrixes. These experiments have been at scales ranging from 1 to 500 litres. This experience has resulted in the evolution of a well developed, reliable, and established experimental procedures for measuring the corrosion of encapsulated metals, which has been used for these trials.

3.1. Provision of uranium pennies

Natural uranium was provided from Westinghouse Chemical & Metallurgical Services (C&MSD) at Springfields and taken from the Magnox fuel manufacturing process. About three Uranium bars from fuel manufacture per week are routinely examined/analysed for grain structure The bars are dissected by C&MSD and the pennies (end sections from the bar) retained. The examination / analysis includes etching with concentrated hydrochloric acid for approximately 60 seconds followed by a 4 second dip in concentrated nitric acid. The samples are then examined under water and finally rinsed in industrial methylated spirit before hot air drying. The samples are then stored until disposal, possibly up to 12 months.

The pennies were cleaned before use by immersion in a solution of $5\%^{w}/_{v}$ citric acid for 5-10 minutes in an ultrasonic bath. The pennies were then thoroughly washed with de-ionised water and re-inserted into the ultrasonic bath and agitated for 5-10 minutes with de-ionised water, this operation was then repeated. The pennies were then dried with a tissue and stored in polythene bags. A typical penny is shown in Figure 1.

Before use the pennies were weighed and the dimensions measured using a digital micrometer. The average dimensions, total weight and surface area of the pennies used in the trials are shown in Table 2.

3.2. Uranium arrangement within the reactor vessel

The reaction vessels used for each trial are cylindrical stainless steel vessels measuring 379 mm high by 294 mm diameter, and therefore having an internal volume of 25.73 litres. The pressure transducer is fitted into the stainless steel reaction vessel lid. A suspension cradle, measuring 340 mm high by 290 mm diameter was manufactured from 3 mm thick stainless steel rods which were used to support plastic netting on which the 30 pennies within each reactor vessel were placed. The pennies were supported from this cradle and were positioned so that there was ample access of the grout to the uranium metal surface to prevent any potential interaction between nearest neighbours. This arrangement was chosen to ensure that all the available metal surface area exposed to grout within each trial. A photograph of the cradle is shown in Figure 2. A thermocouple was also fitted to record the ullage temperature when measuring gas generation. The experiments were designed with only one thermocouple to minimise the number of ports in the reaction vessel. This minimised the risk of leakage which experience had shown was most likely to occur at instrumentation ports.

3.3. Pressure testing the reactor vessels

After loading the reaction vessels with the requisite number of uranium pennies, the grout mixture was prepared and poured into the vessels. The lids were places on the vessels and sealed, the vessels were purged with argon for 10 minutes at 3-5 litres/min before each vessel was pressurised to about 0.3 bar with argon. The pressure was then monitored for several days using a Ptx 1400 pressure transmitter in the reaction vessel lid, to ensure that

the vessel lids had been fitted correctly and a gas tight seal produced. Monitoring the reactor vessel pressures indicated that no leakage from the reactor vessels was occurring.

In addition, as each grout formulation trial was aimed to be undertaken at a constant curing temperature, a wrap around trace heating jacket was placed around each reactor vessel following pressure testing, and this arrangement is shown in Figure 2. The jackets (32 cm by 107 cm) have a maximum operating temperature of 120°C (230 volts, 250 watts rating) and are controlled via a manually operated thermostat.

3.4.   Corrosion studies

The appropriate simulant[3] and grout formulations were prepared and details of each trial are depicted in Table 1.

The grout formulations were prepared in a 'Belle bucket mixer 50 super'. The required volume of de-ionised water was initially added to the bucket, followed by the appropriate quantities of simulant materials and then the encapsulant which were:

1. Ordinary Portland cement (OPC), to EN 197-1, supplied by Castle Cement Ltd, Clitheroe, Lancashire, BB7 4QF
2. Ground granulated blast furnace slag (BFS), to BS 6699, supplied by Castle Cement Ltd, Clitheroe, Lancashire, BB7 4QF
3. PFA, to BS 3892, supplied by Rugby Ash, Drax Power Station, Selby, North Yorkshire, YO8 8PQ
4. Stainless steel AISI 316, less than 45µm, supplied by Goodfellow Cambridge Limited, Ermine Business Park, HUNTINGDON, Cambridgeshire, PE29 6WR, England
5. Haemetite powder, supplied by Hayes Chemicals Distribution, Longshanks Lane, Birtley, Chester Le Street, County Durham, DH3 1QZ.
6. Sand, 90-600µm and 1.18-2.36mm, supplied by David Ball Group Plc, Huntingdon Road, Cambridge, CB3 8HN
7. ADVA® Cast 550 superplasticiser. Material is carboxylated poly-ether comb polymer, supplied by Grace Construction Products Limited, 852 Birchwood Boulevard, Birchwood, Warrington, Cheshire WA3 7QZ, United Kingdom
8. Cenospheres, supplied by Minelco Specialities Ltd, Raynesway, Derby, DE21 7BE, England.
9. Barium peroxide 95%, supplied by Fisher Scientific UK Ltd, Bishop Meadow Road, Loughborough, Leicestershire, LE11 5RG

Mixing of the grout was maintained throughout powder addition and for several minutes afterwards to ensure that a fully homogenised grout was obtained. The grout was then transferred from the 40-litre drum by pouring the grout into the vessel before lidding. Table 3 shows the weights of the different components added to the grout mix and Table 4 shows the overall water and solids content of the grout mixes expresses using a range of measures.

After grout infill each reactor vessel was purged with works argon at 3-5 litres/min for five minutes. Each vessel was then subjected to a leak test where the pressure in the vessel was monitored for at least 24 hours at about 20°C under a typical pressure. The leak testing was carried out to ensure that when the temperature was increased to 60°C and hydrogen was

generated good quality reliable data would be generated which was not compromised by leakage from the system. The temperature was kept low to ensure that the uranium corrosion would remain in its incubation period so that no corrosion would occur during this leak testing phase. The samples took two days to prepare so the first day's samples were tested for two days and the second day's tested for one day before all the temperature of all the trials were simultaneously increased.

3.5. *Monitoring of the reactor vessels*

The pressure and temperature readings were logged automatically at 30 minute intervals using a Solartron Mowbray modular data logging system.

3.6. *Pressure transducer methodology*

The corrosion of uranium in each encapsulated product was monitored by measuring the pressure and temperature of the gas in each reactor vessel, every 30 minutes. The volume of gas generated could then be obtained by knowing:
- the ullage volume in each reactor vessel (calculated theoretically from knowing the volumes of the reactor vessel, amount of grout added and uranium pennies)
- and using the gas law to calculate the number of moles of gas present in that volume, at the particular temperature measured i.e.,
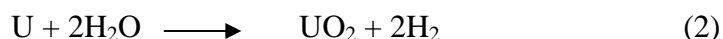
$$PV = nRT \qquad (1)$$

where
- P = gas pressure
- n = number of moles of gas
- T = temperature
- V = gas volume
- R = gas constant

The number of moles of gas generated could then be converted into a weight of uranium corroded based on the equation:

$$U + 2H_2O \longrightarrow UO_2 + 2H_2 \qquad (2)$$

Therefore using this principle either the number of moles or litres of hydrogen evolved or weight of uranium corroded can be plotted against time. The rate of change of these responses was also calculated over 24 hours from the change over the previous and subsequent 12 hours to give a corrosion rate.

The pressure inside each reactor vessel was released at regular intervals via the second ball valve, typically when the pressure had attained 1200-1300 mbar to avoid excessive pressure build up and minimise the effect of any slight leakage. Pressure readings before and after venting allowed the cumulative record to be adjusted for continuity on each occasion.

Monitoring was started from the time the temperature was increased from the ambient of about 20°C at which the leak testing had been carried out. This was between one and two days after the samples had been originally encapsulated.

3.7.   Grouts investigated

The following grouts were investigated:

1. KW Basin North Load Out Pit simulant 75:25 PFA/OPC Superplasticiser
2. KW floor / pit & settler in 75:25 PFA/OPC Superplasticiser
3. KW KOP 75:25 PFA/OPC Superplasticiser
4. KE Blend 75:25 PFA/OPC Superplasticiser
5. KE Blend 80:20 BFS/OPC Superplasticiser
6. KE Blend 100% OPC Superplasticiser & Cenospheres
7. KE Blend 75:25 PFA/OPC Superplasticiser & Barium Peroxide
8. KE Blend 75:25 PFA/OPC Superplasticiser
9. KE Blend 100% OPC Superplasticiser
10. KE Blend 80:20 BFS/OPC No additives

A PFA/OPC grout is used as in the longer term this blend will have a lower permeability than a purely OPC grout and will also not remove oxygen unlike a BFS/OPC grout[4]. This removal of oxygen by BFS based systems is due to the presence of sulphide compounds inn the BFS which will react to form sulphates. The removal of oxygen from the system will result in a reduction of the induction period prior to the commencement of hydrogen generation during corrosion.

Trials 1 to 4 assess the effect on the corrosion rate of the different waste compositions.

Trials 5 and 10 use a BFS/OPC grout to extend the data already existing for BFS/OPC grouts from w/c ratios of 0.31 to 0.40, which did not contain any waste simulant, down to the 0.21 that can be achieved with superplasticiser and waste included. This data will allow correlation between the corrosion data at high water content with BFS/OPC and the data generated with other blends.

Trials 6 investigates the effect of adding cenospheres and trial 7 investigates the effect of having a source of oxygen available by the addition of barium peroxide.

Cenospheres are hard-shelled hollow spheres with particles sizes from 50 to 200μm. They have a wall thickness of about 10% of their radius.
Cenospheres were chosen for use in the Hanford K Basins encapsulation for a combination of reasons. As mentioned above the microspherical shape improves the rheology of a grout mix in that the shape acts to "lubricate" the mix. This will allow a lower water content to be used in the mix thus reducing the water available for corrosion of the uranium present in the real waste.

Secondly as the cenospheres are hollow they act to introduce air, present in the spheres, into the cementitious matrix in a controlled amount. This is a controlled way of introducing oxygen into the matrix which may act to increase the induction period.

Barium peroxide was considered because it is known to decompose releasing oxygen which will increase the period prior to the hydrogen generation

Trial 8 extends the data to include an intermediate w/c ratio and trial 9 assesses the effect of a simple OPC only encapsulant.

4. Results

Figure 4 to Figure 23 show the cumulative percentage uranium corrosion and uranium corrosion rate in grams of uranium corroded per day per metre squared (g/m^2/day) plotted against time for each trial. The temperature profiles as measured from the thermocouples in the upper centre of each product are also shown.

These plots have been derived from calculating the number of moles of hydrogen evolved from each test by use of equation 1 from measurement of the pressure change and internal temperature (detected from the internal thermocouple) within each reactor vessel at a given time period. This value was then be converted to a weight of uranium corroded by assuming that the principal reaction occurring between the alkaline cement pore solution and uranium metal is that depicted in equation 2.

The corrosion rate measured was then converted to a rate per unit area of uranium by calculating the total surface area available for corrosion in the reaction vessel. As the metal corrodes the total surface area will decrease, this change was included in the calculation by removing the uranium corroded from the surface of each penny assuming the vessel was made up from equal average sized pennies to give a new total surface area.

The figures showing the corrosion rate against time were then used to generate data points of corrosion rate against temperature which are plotted in Figure 24 and Figure 25 for the trials without barium peroxide. In some cases it was possible to generate more than one rate and temperature correlation per trials where the temperature control had held at a different temperature for a significant period of time during the set up of the experiments. An example of this is particularly apparent in the results of trial H5 at 8 and 14 days. Data from the early period of corrosion up to seven days were not used to as the corrosion rates had not settled down to reflect the observed curing temperature before the temperature was readjusted to be closer to the required 60°C.

The best fit line in Figure 25 converted to natural logs is given by

$$\text{Ln rate} \quad = \quad \underline{\frac{-8679.9}{\text{Temperature (K)}}} \quad + \quad 29.227 \qquad g/m^2/\text{day}$$

The activation energy can be calculated from this expression and is 72 kJ/mole.

5. Discussion

5.1. Incubation period

All the trials apart from the one trial dosed with barium peroxide have completed their incubation period. The incubation period lasted approximately 2 days from the time the

curing temperature was increased to 40°C which is consistent with previous corrosion trials in a cement matrix[1].

The trial containing barium peroxide was designed to have an extended incubation period through the peroxide decomposing to provide a source of oxygen. This has been achieved with the incubation period extending up to ten days. During this period some pressure increases were observed. However, these gas releases were associated with the changes in curing temperature with the rate of change quickly reducing back to zero and hence are probably artefacts of these temperature changes. Further extension of this incubation period could be achieved by dosing with increased levels of peroxide.

5.2.   Corrosion rates

During the first eleven days there have been several changes in the curing temperature as the heating surrounding the vessels was adjusted to give a 60°C curing temperature. After seven days the adjustments were infrequent and the corrosion rates had settled down to give a constant rate depending on the temperature.

5.2.1. Effect of barium peroxide

One trial was carried out with barium peroxide to provide a source of oxygen to prevent the generation of hydrogen. As discussed above Figure 16 and Figure 17 show that this had been successful with the onset of hydrogen generation or the incubation period being extended to about ten days compared to about two days for the rest of the trials. After this the corrosion rate has gradually increased for the next week to approach that of the other trials.

The amount of barium peroxide added was selected to test the concept and has not been optimised. Therefore, this effect could be extended by using higher loadings of peroxide. It is possible that it could be extended to time periods which could be beneficial if the products were to be immediately transported to WIPP. However, it is unlikely that the effect could be extended to times long enough to be of any use in this situation if the waste is stored for any time at CWC before transportation to WIPP.

5.2.2. Effects of solids content of waste form

All the encapsulants apart from the trial dosed with barium peroxide have shown similar behaviour. So that any temperature effects can be removed and all the data can be compared with the data generated in BFS/OPC[1] grouts graphs have been generated in which normalised[*] data is plotted against the water cement and water solids contents in various forms. These are shown in Figure 26 to Figure 29. Figure 26 which plots the normalised rate against the water cement ratio, i.e. weight of water divided by weight of PFA, BFS and OPC. This show that between a w/c ratio of 0.4 and 0.21 there is a reduction of rate of about

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[*] The data was normalised by using the rate expression generated in NSTS 4992 to generate a corrosion rate at the temperature of the data point. The observed rate was then divided by the calculated rate to give a normalised rate. A value of one means that the rate was the same and a value of 0.5 means that the rate has been halved.

0.4. However, comparison of trial H10, which is essentially a repeat of the data in NSTS (04) 4992[1], except using a KE blend stimulant instead of water, shows that this is an oversimplification as the corrosion rate still decreases by a factor of 0.4 despite the w/c ratio remaining the same.

In Figure 27 to Figure 29 the corrosion rate is plotted against the solids content of the encapsulating matrix expressed in terms of:

- The ratio of weight water divided by the total weight of solids in the grout (not including the uranium pennies) i.e. w/s ratio.
- The percentage of solids by weight, i.e. weight solids divided by the total weight of solids (not including uranium pennies) plus water.
- The percentage of solids by volume, i.e. weight solids divided by the total volume of solids (not including uranium pennies) plus water.

These show that the decrease in corrosion rate is best described by the volume fraction of solids present in the grout mix. However, due to the inherent variability in the results, using the w/s ratio or percentage solids by weight, which are simpler to calculate, also give an adequate correlation. It is not unexpected that the rate is dependent on the total solids in the grout, as the corrosion rate will depend on the ability of water to access the uranium. Increasing the solids content of the grout will reduce the area over which water can access the uranium and hence reduce the corrosion rate. When the corrosion rate is compared with the w/c ratio, i.e. the water divided by the weight of cement powders this takes into account the water removed by hydration and some of the effects of increased solids content but doesn't pick up the solids included in the waste. Using the total solids content gives a better correlation as both the effects are captured. As the overall availability and transfer of water for corrosion is a volume effect rather that a mass effect using the volume ratio of solids to water gives the best correlation particularly when the density of the solids varies significantly.

Therefore reducing the water content of the grout reduces the corrosion rate of the uranium and the reduction is proportional to the total solids content of the grout rather than purely the cement content.

5.2.3. *Effect of temperature*

For the trials without barium peroxide a correlation of corrosion rate against temperature has been generated which is:

$$\text{Ln rate} \quad = \quad \underline{\frac{-8679.9}{\text{Temperature (K)}}} \quad + \quad 29.227 \qquad \text{g/m}^2\text{/day}$$

The activation energy can be calculated from this expression and is 72 kJ/mole. This relationship has been generated over the range of about 55 to 65°C. Figure 30 shows a comparison between this rate equation and that generated previously in a higher water content BFS/OPC grout[1]. Comparing the rate expressions shows that there has been a

reduction in rate due to the lower water content of the grout of about 0.4 at 60°C reducing to 0.5 at about 25°C.

This rate expression was generated with data over a range of about 55 to 65°C. Whist it is expected that the reduction in rate should still apply at lower temperatures this should be confirmed by measurement of the corrosion rate at lower temperatures. This could be readily carried out by reducing the temperature of the existing trials for a suitable period. Initial examination of the existing data during the first week or so of corrosion suggests that there may be suitable data points which could be used to extend the temperature range. The use of these points is not recommended however, as over this period the temperatures had never stabilised sufficiently for the rates to settle to the true rate for that temperature before the temperature was readjusted to be closer to the target 60°C curing temperature. Therefore, the use of data generated in this time period could be misleading.

5.2.4. Change in corrosion rate with time

For the trials without barium peroxide the corrosion rates have settled to a constant rate appropriate to the corrosion temperature. It is not expected that this rate will increase as the samples appear to be well past the incubation period. However there may still be some decrease in rate observed over the next few weeks. This is because these samples have a very low water content and over this time period further cement hydration will occur, particularly for the samples containing PFA where there will be an ongoing pozzolanic reaction. Therefore, as the water contents are already very low then further loss of water may reduce the corrosion rate further.

5.3. Application of results to KE and KW wastes encapsulation

Whilst there is a relationship between the water to total solids ratio and the corrosion rate, Figure 27 to Figure 29 show that due to the scatter in results for these trials and those in high water content BFS/OPC[1] there are likely to be two corrosion scenarios for KE and KW waste encapsulated in cement:

- A high corrosion rate which is equivalent to that of uranium in water which occurs in high water and low solids content grouts. As the higher water content means that less cement powders are added these products will also have the highest waste loadings in the absence of any other restrictions.

- A lower corrosion rate which is a factor of 0.4 to 0.5 (depending on the temperature) of the high rate. This requires a higher solids and lower water content in the grout so these product will have lower waste loadings in the absence of any other restrictions. The encapsulation grout selected within this region appears to have little significance unless an additive is included to produce oxygen in which case a PFA/OPC grout should be used.

Modelling studies of the hydrogen generation from encapsulated KE and KW wastes should therefore use the following expression to model scenarios where a formulation is selected to maximise the uranium corrosion rate:

Ln rate $=\dfrac{-9298.1}{\text{Temperature (K)}}+$ 32.008 $\text{g/m}^2\text{/day}$ (3)

Where the scenario being modelled uses a grout selected to minimise corrosion this expression should be used for the uranium corrosion rate:

Ln rate $=\dfrac{-8679.9}{\text{Temperature (K)}}+$ 29.227 $\text{g/m}^2\text{/day}$ (4)

Figure 31 and Figure 32 give an indication of the rate of change of radius of 250, 500 and 1000 micron particles of uranium corroding at 20, 40 and 60°C using these two rate expressions.

Figure 26 to Figure 29 give an indication of the scatter associated with these results. These indicate that for a sensitivity analysis a maximum rate is likely to be less than twice and the minimum is likely to be about 0.2 of that in equation 3. These ratios should be applied to the corrosion rates predicted by equation 3 to assess the sensitivity of the model to the variability in corrosion rate.

6. Conclusions

Increasing the total solids content and reducing the water content of the grout has reduced the corrosion rate of uranium to a factor of about 0.4 at 55 to 65°C. Data is required to confirm this reduction is still applicable at lower temperatures.

Modelling studies of the hydrogen generation from encapsulated KE and KW wastes should use the following expression to model scenarios where a formulation is selected to maximise the uranium corrosion rate:

Ln rate $=\dfrac{-9298.1}{\text{Temperature (K)}}+$ 32.008 $\text{g/m}^2\text{/day}$ (3)

Where the scenario being modelled uses a grout selected to minimise corrosion this expression should be used for the uranium corrosion rate:

Ln rate $=\dfrac{-8679.9}{\text{Temperature (K)}}+$ 29.227 $\text{g/m}^2\text{/day}$ (4)

The maximum rate is likely to be less than twice and the minimum is likely to be about 0.2 of that in equation 3. These ratios should be applied to the corrosion rates predicted by equation 3 to assess the sensitivity of the model to the variability in corrosion rate.

7. Recommendations

The expression given above are used to model the corrosion of uranium in packages of encapsulated KE and KW basing wastes.

Monitoring of the samples should be continued at least until hydration is complete to measure any further reduction in rate caused by this hydration. During this continued monitoring the curing temperature should be reduced at a suitable time to generate corrosion rate data at lower temperatures.

8. References

1 NSTS (04) 4992 BNFL Historical Data on the Corrosion of Uranium in BFS/OPC Cement in Support of Treating Hanford KE and KW Basin Wastes Using Cementation. I. H. Godfrey, et al.
2 NSTS (04) 4991 Inactive Grouting Trials in Support of Treating Hanford KE and KW Basin Wastes Using Cementation. S. Rawlinson, et al.
3 NSTS (04) 4990 Review of Sampling Data and Simulant Definition for Trials Investigating Treating Hanford KE and KW Basin Wastes Using Cementation. S. Rawlinson, et al.
4 Cement Chemistry 2nd edition H.W.F. Taylor ISBN: 0 7277 2592 0

Table 1 Grout composition and curing temperature for corrosion trials

Trial	Simulant	Cementitious material	Blend	Additive	W/C ratio	Temperature
1	KW NLOP	PFA /OPC	75:25	Superplasticiser	0.21	60°C
2	KW floor / pit & settler	PFA /OPC	75:25	Superplasticiser	0.21	60°C
3	KW KOP	PFA /OPC	75:25	Superplasticiser	0.21	60°C
4	KE Blend	PFA /OPC	75:25	Superplasticiser	0.21	60°C
5	KE Blend	BFS/OPC	80:20	Superplasticiser	0.21	60°C
6	KE Blend	OPC	100%	Superplasticiser & Cenospheres	0.21	60°C
7	KE Blend	PFA /OPC	75:25	Superplasticiser & Barium Peroxide	0.21	60°C
8	KE Blend	PFA /OPC	75:25	Superplasticiser	0.28	60°C
9	KE Blend	OPC	100%	Superplasticiser	0.21	60°C
10	KE Blend	BFS/OPC	80:20	None	0.31	60°C

Table 2 Uranium content of corrosion trials

Reactor vessel	Number of "pennies"	Average thickness (mm)	Average diameter (mm)	Total mass (g)	Total surface area (mm^2)
H1	30	10.79	28.01	3563	65516
H2	30	12.77	28.66	4399	73215
H3	30	12.33	28.68	4289	72089
H4	30	11.07	28.14	3693	66787
H5	30	12.80	28.63	4439	73185
H6	30	12.84	28.69	4482	73516
H7	30	10.56	27.87	3445	64425
H8	30	12.83	28.81	4527	73971
H9	30	12.65	28.65	4382	72876
H10	30	12.50	28.82	4403	73106

Table 3 Simulant and grout composition

Trial	Waste	Water	Stainless steel	Sand PSD 1.18-2.36 mm	Sand PSD 90-600 µm.	Haematite	Sand PSD 90-150µm	OPC	PFA	BFS	ADVA 550	Cenospheres / barium peroxide
		g	g	g	g	g	g	g	g	g	g	g
H1	NLOP	6750	540	5850	-	342	-	8450	25300	-	337.5	-
H2	KW floor pit and settler	6150	13200	803	2460	1640	-	7700	23050	-	307.5	-
H3	KW KOP	5621	-	22100	-	-	-	7000	21100	-	281	-
H4	KE blend	6150	836	1276	3696	820	1640	7700	23050		307.5	-
H5	KE blend	6750	918	1400	4752	900	1800	6750	-	27000	337.5	-
H6	KE blend	7125	969	1478	5016	950	1900	35650	-	-	356.5	712.5 Cenospheres
H7	KE blend	6450	877	1338	4540	860	1720	8000	24200	-	322	400 Barium peroxide
H8	KE blend	7500	1020	1556	4858	1000	2000	6900	20700	-	276	-
H9	KE blend	7125	969	1478	5016	950	1900	35625	-	-	356.25	-
H10	KE blend	8250	1122	1712	5808	1100	2200	5325	-	21300	-	-

Note. These amounts are not precisely the same as those found in NSTS (04) 4990. In each case the weight percentage of simulant components is however the same.

Table 4 Ratios of solids to water in corrosion trials

Trial	Waste	By weight				By volume			
		w/c^1	w/s^2	% cement^3	% solids^4	w/c^1	w/s^2	% cement^3	% solids^4
H1	NLOP	0.21	0.17	71	85	0.52	0.44	59	69
H2	KW floor pit and settler	0.21	0.13	56	88	0.52	0.41	56	71
H3	KW KOP	0.21	0.12	50	89	0.52	0.30	44	77
H4	KE blend	0.21	0.16	68	86	0.52	0.42	57	70
H5	KE blend	0.21	0.16	67	86	0.61	0.47	53	68
H6	KE blend	0.21	0.16	66	86	0.65	0.46	49	68
H7	KE blend	0.21	0.16	66	86	0.52	0.41	56	70
H8	KE blend	0.28	0.20	60	83	0.70	0.53	49	65
H9	KE blend	0.21	0.16	67	86	0.65	0.50	51	67
H10	KE blend	0.31	0.21	57	82	0.91	0.63	42	61

1 - w/c is the weight or volume of water divided by the weight or volume of cement powders (BFS, OPC or PFA)

2 - w/s is the weight or volume of water divided by the total weight or volume of solids (i.e. simulant plus BFS, OPC or PFA and additives)

3 - % cement is the weight or volume of cement powders (BFS, OPC or PFA) divided by the total weight or volume of cement powders (BFS, OPC or PFA), plus simulant and water

4 - % solids is the weight or volume of solids (i.e. simulant plus BFS, OPC or PFA and additives) divided by the total weight or volume of solids (i.e. simulant plus BFS, OPC or PFA and additives) and water

Figure 1 Typical uranium penny

Figure 2 Arrangement of cradle for U pennies

Figure 3 Corrosion monitoring vessel

Figure 4 Cumulative corrosion for Trial 1 - KW Basin NLOP, 3:1 PFA/OPC, S/P, 0.17 w/s ratio by weight, 60°C cure
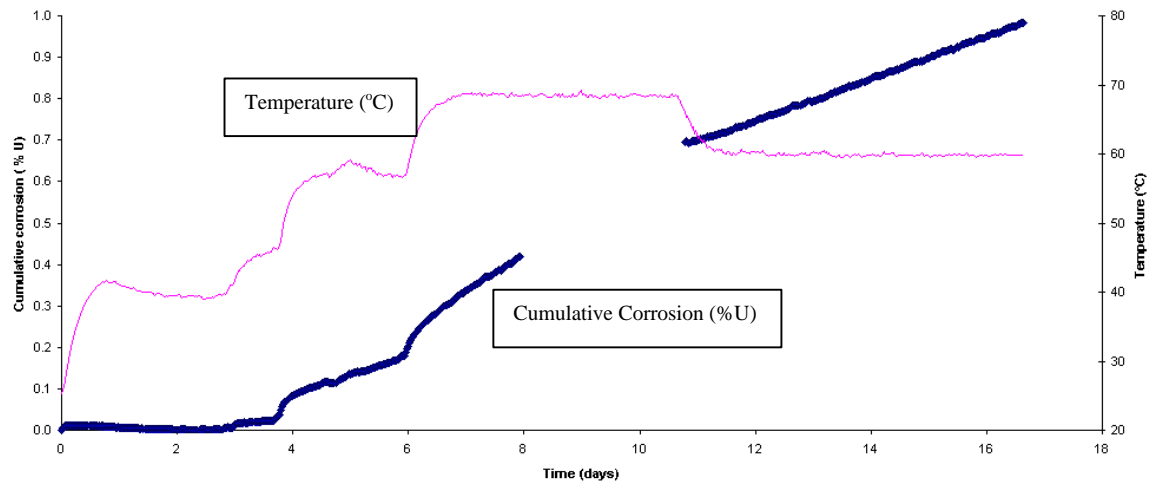
**Figure 5 Corrosion rate for Trial 1 - KW Basin NLOP, 3:1 PFA/OPC, S/P, 0.17 w/s ratio by weight, 60°C cure**
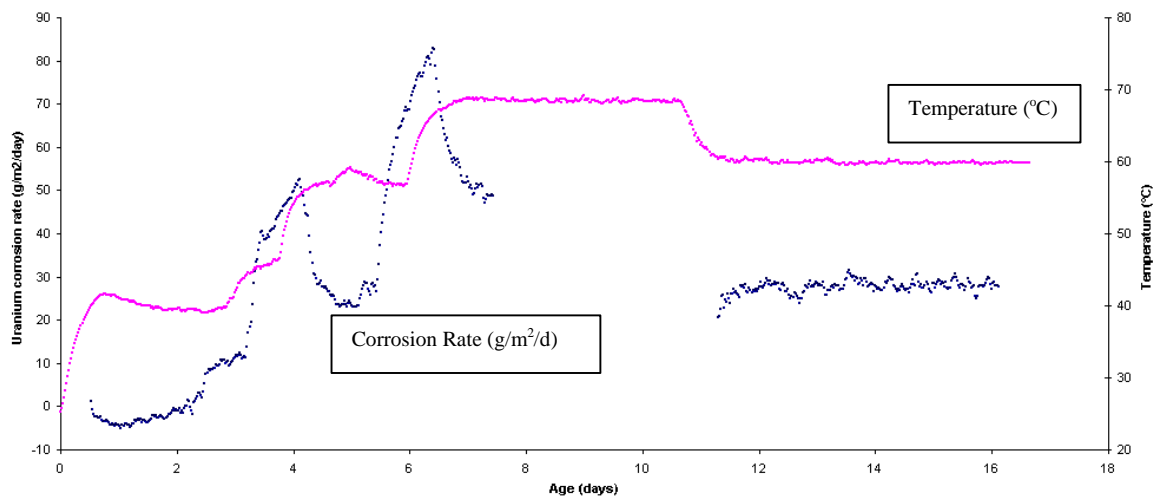
Figure 6 Cumulative corrosion for Trial 2 - KW floor / pit /settler, 3:1 PFA/OPC, S/P, 0.13 w/s ratio by weight, 60°C cure
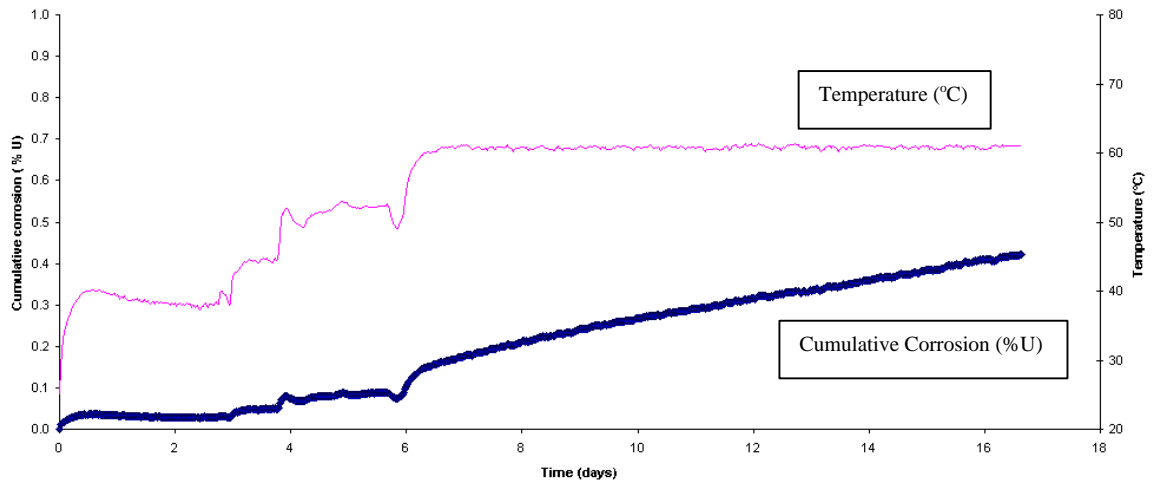
Figure 7 Corrosion rate for Trial 2 - KW floor / pit / settler, 3:1 PFA/OPC, S/P, 0.13 w/s ratio by weight, 60°C cure
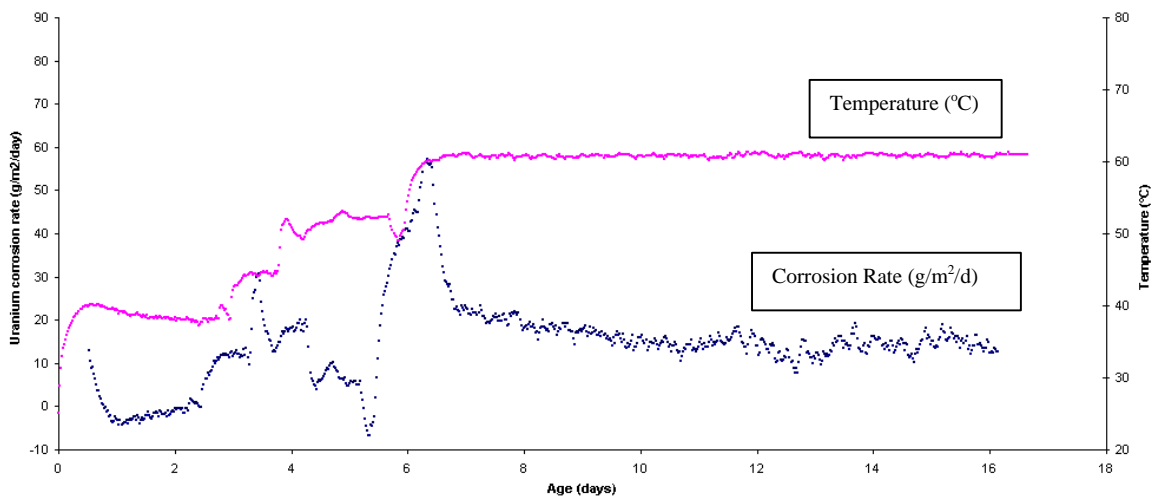
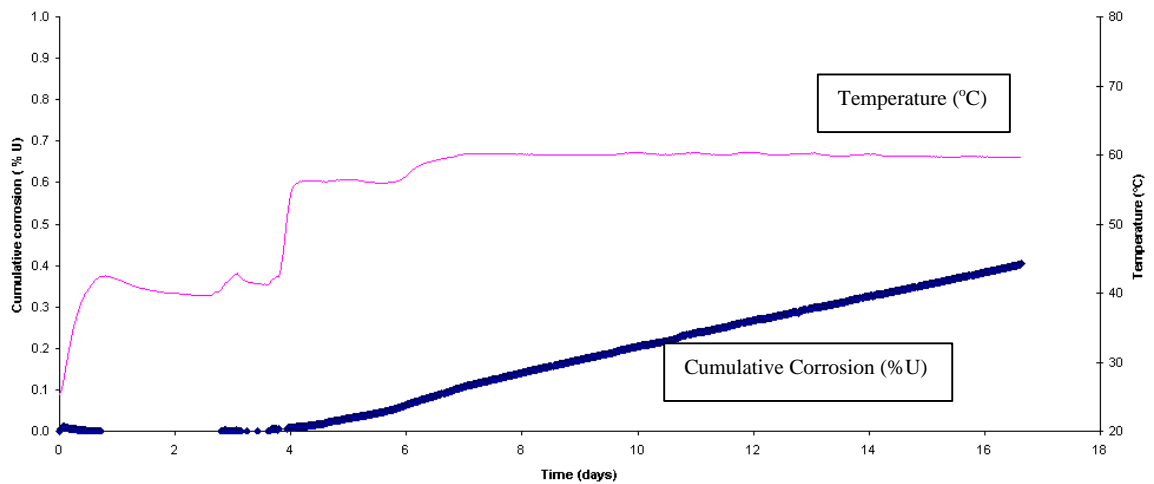**Figure 8 Cumulative corrosion for Trial 3 - KW KOP, 3:1 PFA/OPC, S/P, 0.12 w/s ratio by weight, 60°C cure**
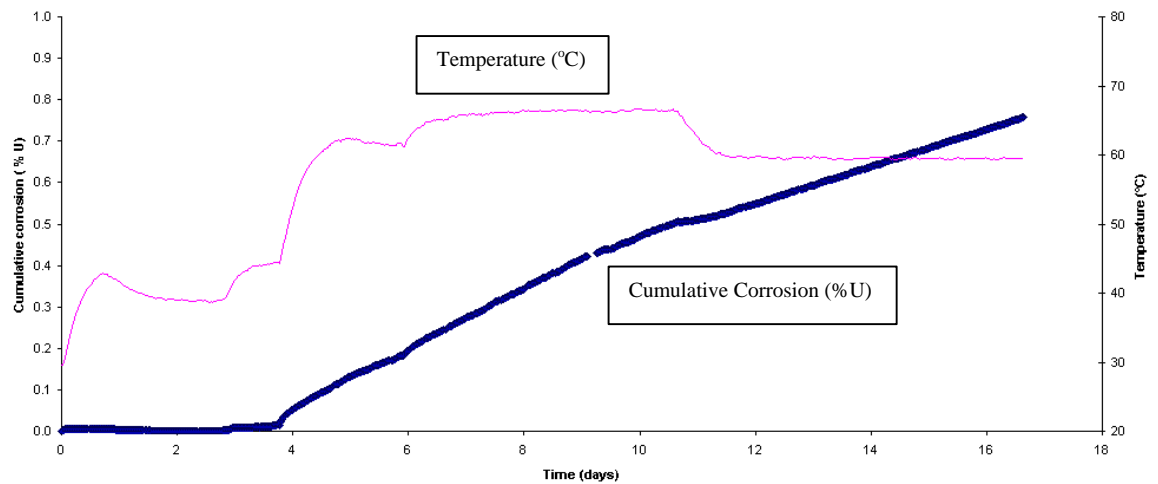
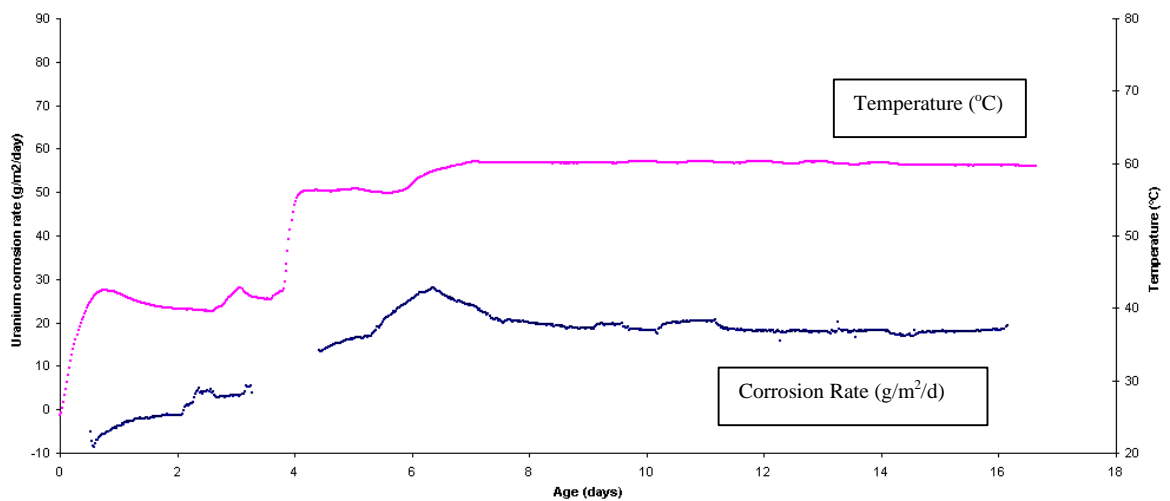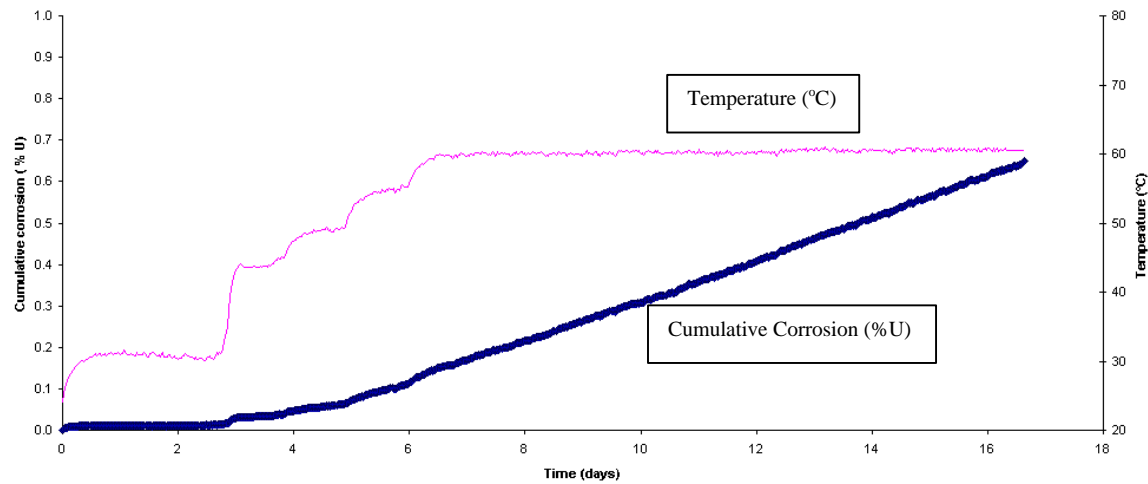**Figure 9 Corrosion rate for Trial 3 - KW KOP, 3:1 PFA/OPC, S/P, 0.12 w/s ratio by weight, 60°C cure**
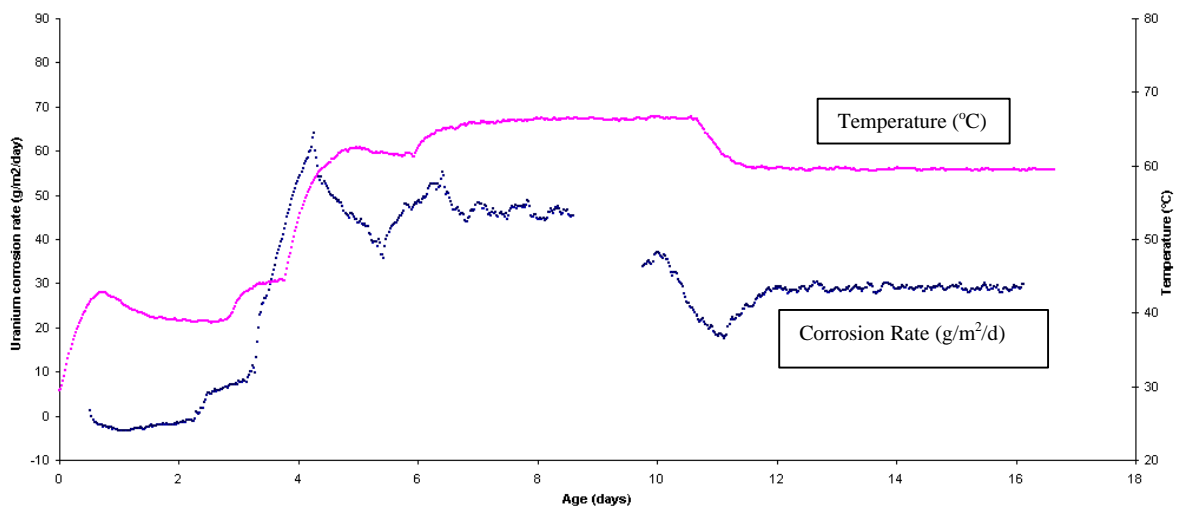
Figure 10 Cumulative corrosion for Trial 4 – KE Blend, 3:1 PFA/OPC, S/P, 0.16 w/s ratio by weight, 60°C cure
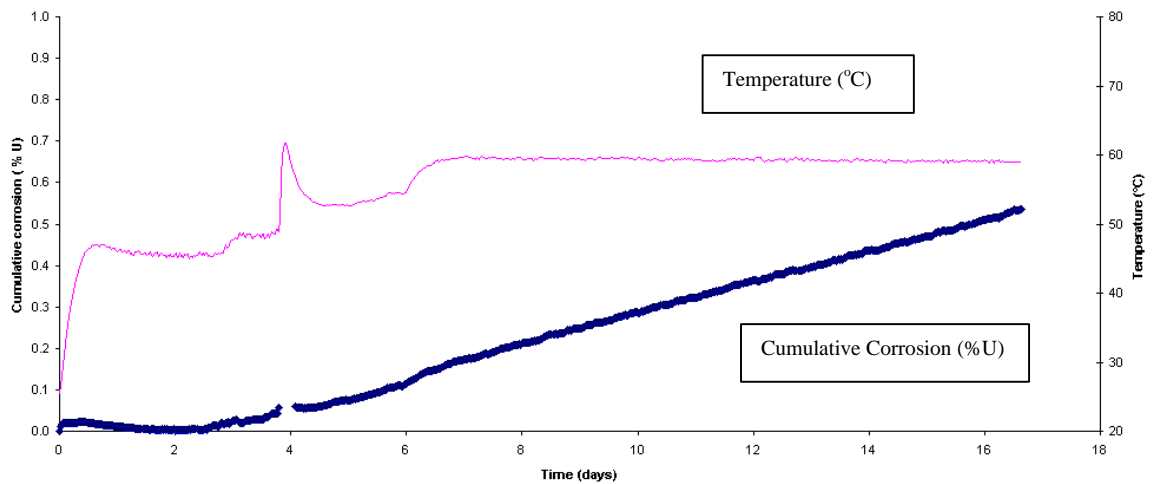
Figure 11 Corrosion rate for Trial 4 – KE Blend, 3:1 PFA/OPC, S/P, 0.16 w/s ratio by weight, 60°C cure
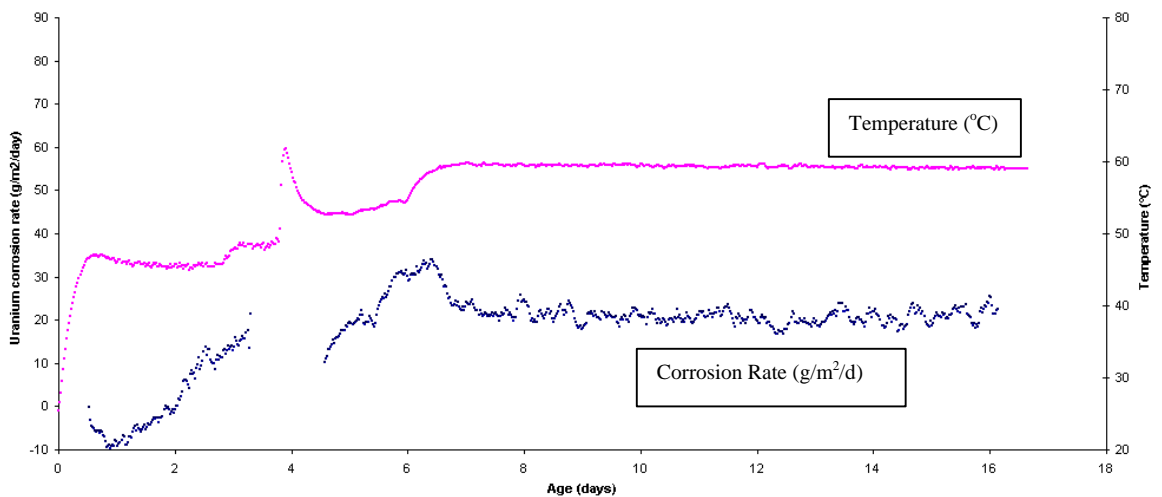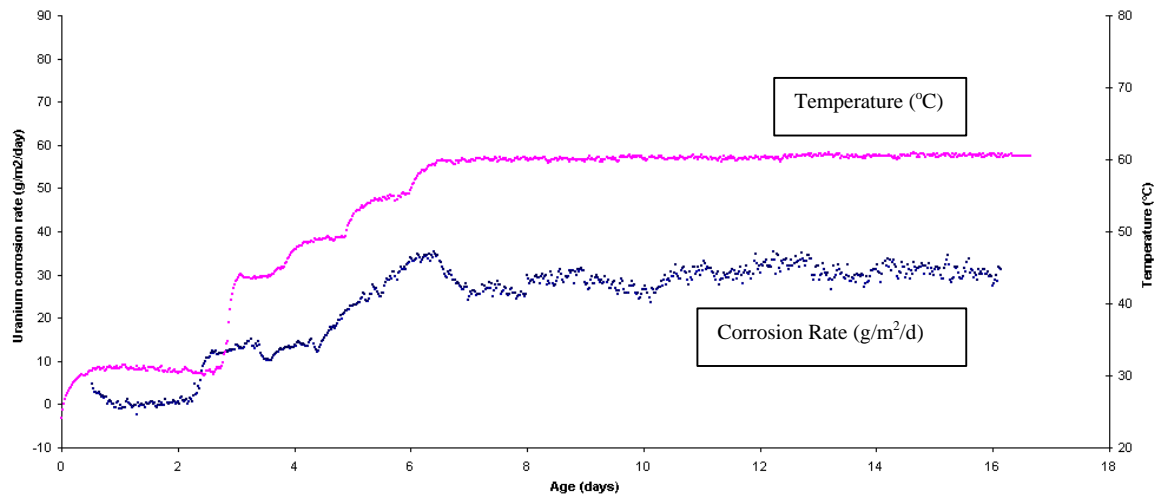
**Figure 12 Cumulative corrosion for Trial 5 – KE Blend, 4:1 BFS/OPC, S/P, 0.16 w/s ratio by weight, 60°C cure**
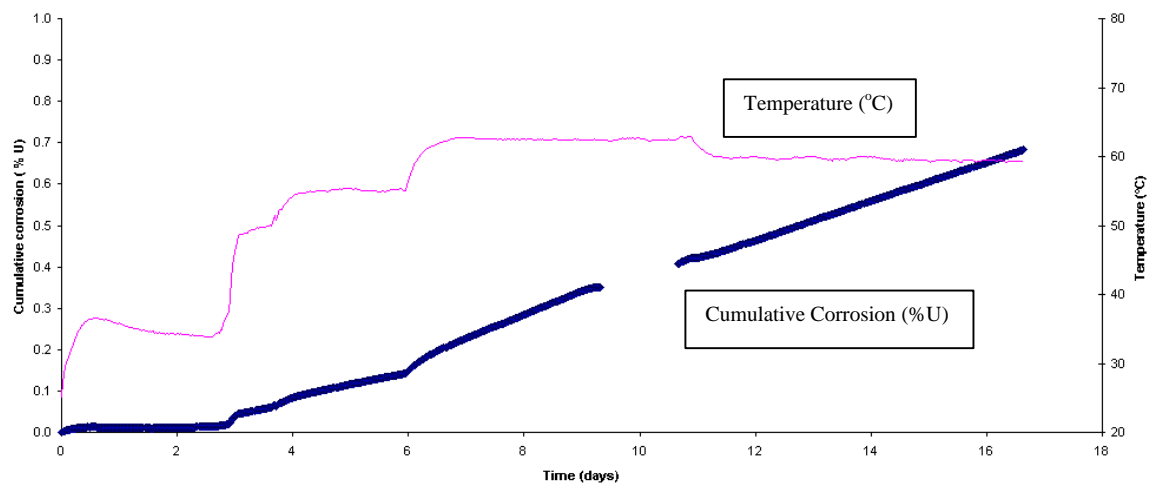
**Figure 13 Corrosion rate for Trial 5 – KE Blend, 4:1 BFS/OPC, S/P, 0.16 w/s ratio by weight, 60°C cure**
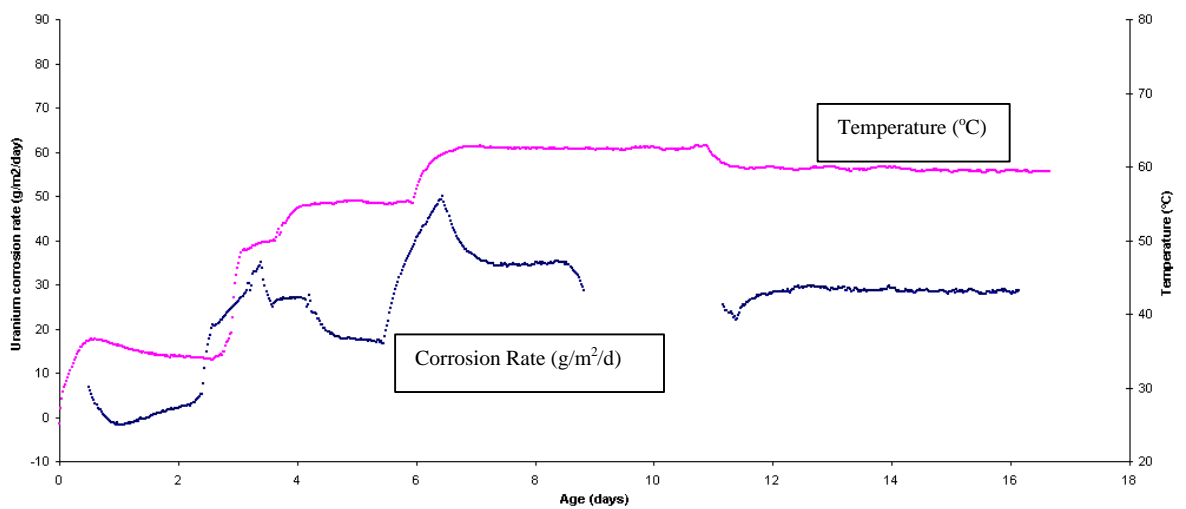
**Figure 14 Cumulative corrosion for Trial 6 - KE Blend, 100% OPC, S/P &
Cenospheres, 0.16 w/s ratio by weight, 60°C cure**
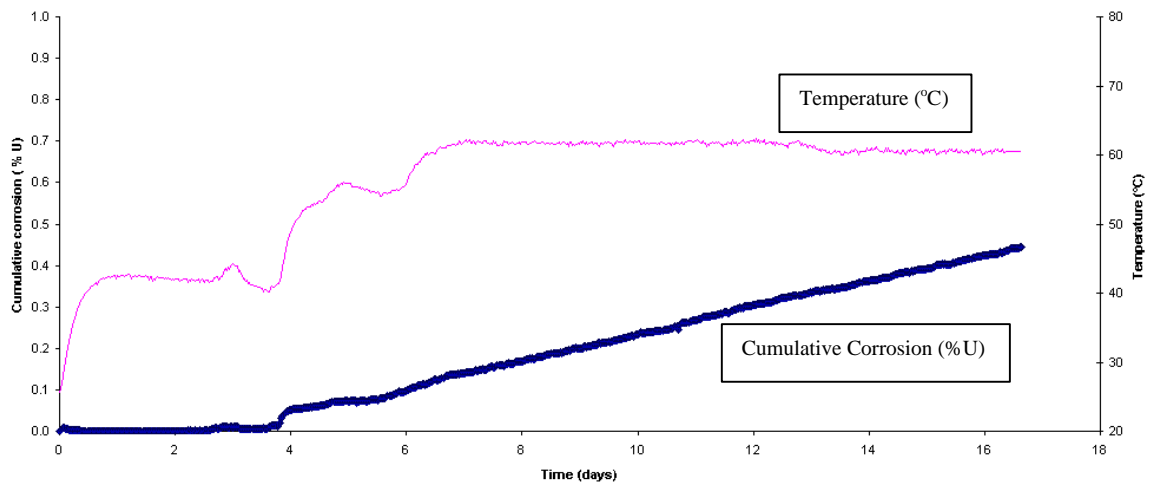
**Figure 15 Corrosion rate for Trial 6 - KE Blend, 100% OPC, S/P & Cenospheres, 0.16
w/s ratio by weight, 60°C cure**
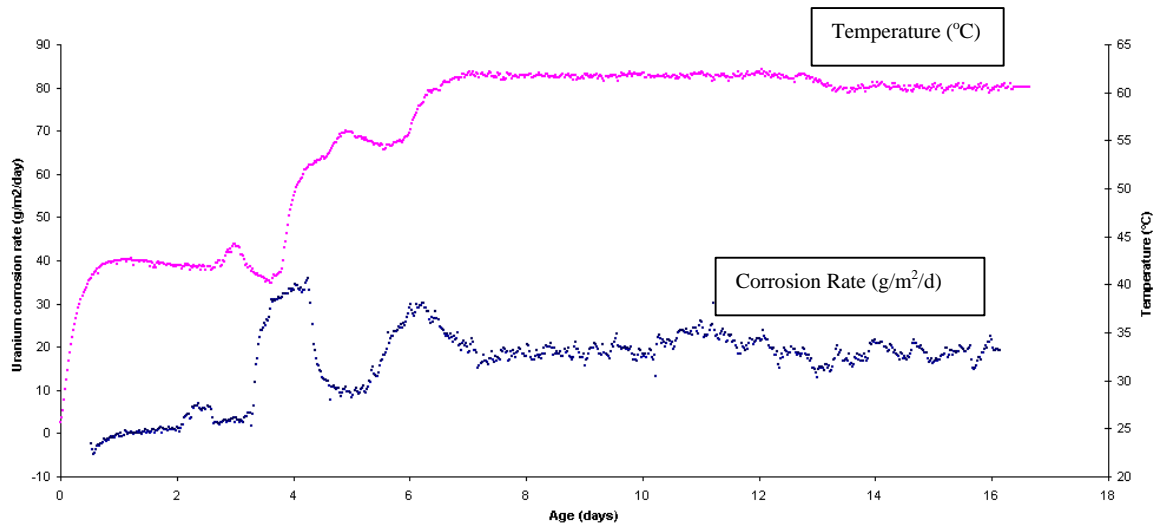
Figure 16 Cumulative corrosion for Trial 7 - KE Blend, 3:1 PFA/OPC, S/P & Barium Peroxide, 0.16 w/s ratio by weight, 60°C cure
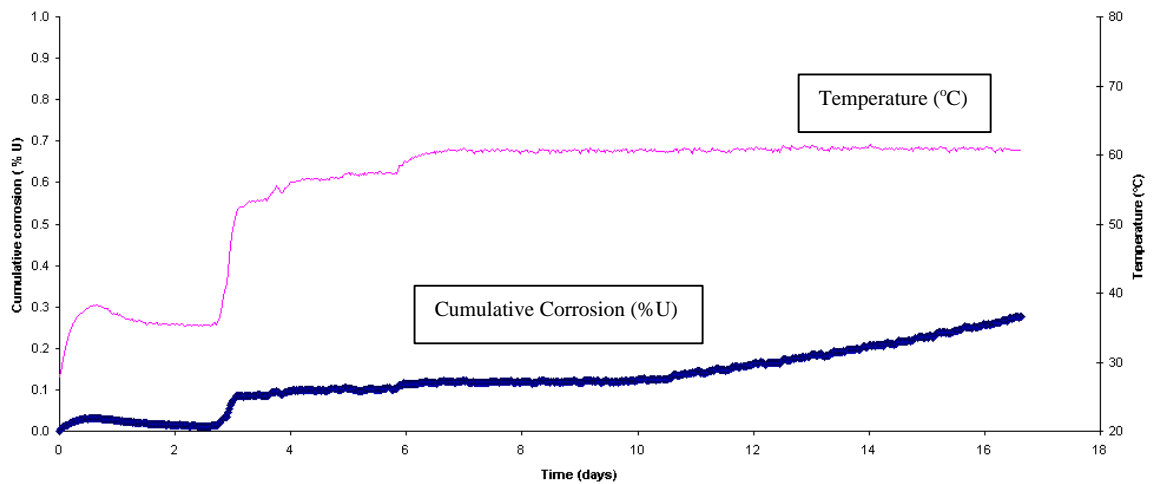
Figure 17 Corrosion rate for Trial 7 - KE Blend, 3:1 PFA/OPC, S/P & Barium Peroxide, 0.16 w/s ratio by weight, 60°C cure
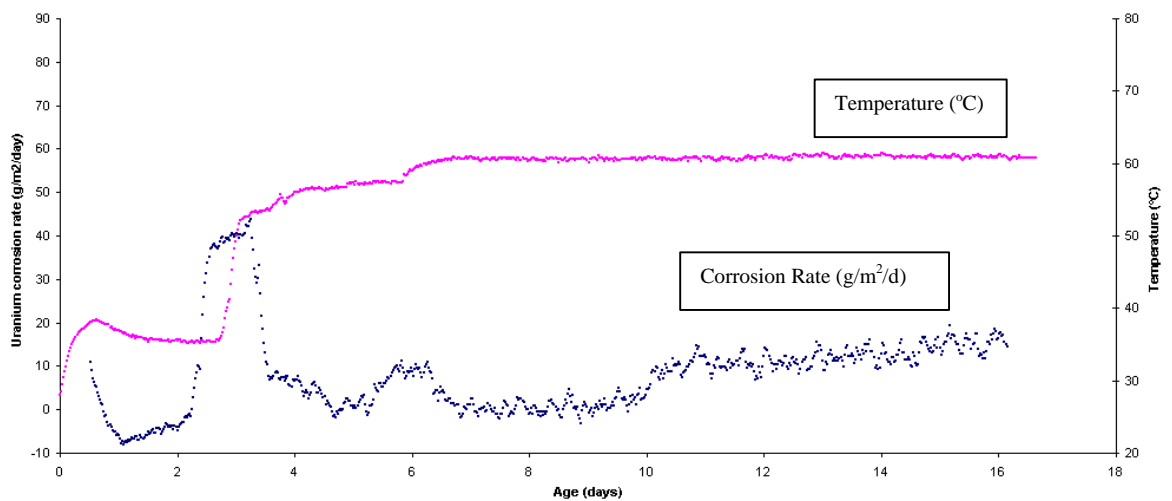
Figure 18 Cumulative corrosion for Trial 8 - KE Blend, 3:1 PFA/OPC, S/P, 0.20 w/s ratio by weight, 60°C cure

Figure 19 Corrosion rate for Trial 8 - KE Blend, 3:1 PFA/OPC, S/P, 0.20 w/s ratio by weight, 60°C cure

Figure 20 Cumulative corrosion for Trial 9 - KE Blend, 100% OPC, S/P, 0.16 w/s ratio by weight, 60°C cure

Figure 21 Corrosion rate for Trial 9 - KE Blend, 100% OPC, S/P, 0.16 w/s ratio by weight, 60°C cure

Figure 22 Cumulative corrosion for Trial 10 - KE Blend, 4:1 BFS/OPC, no S/P, 0.21 w/s ratio by weight, 60°C cure
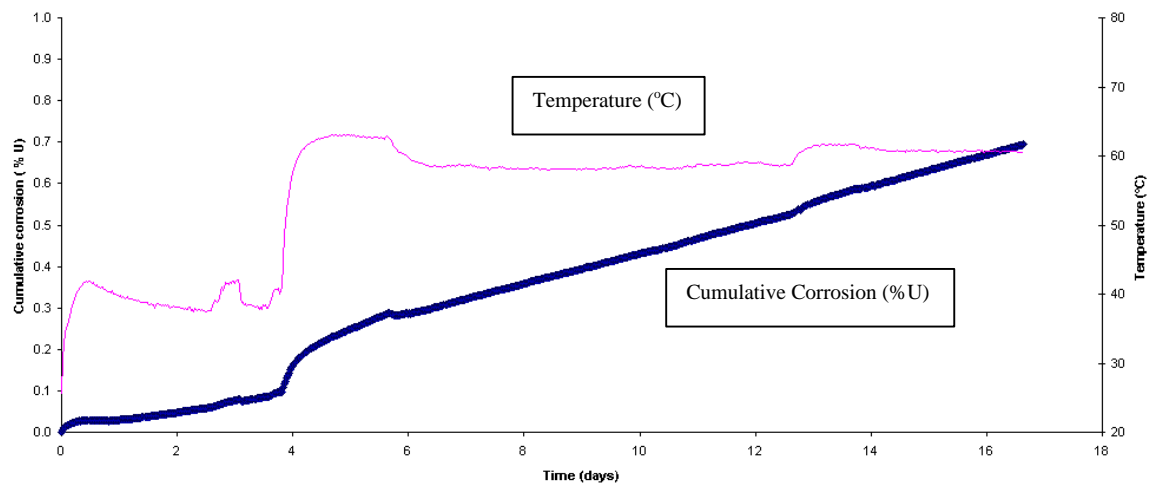
Figure 23 Corrosion rate for Trial 10 - KE Blend, 4:1 BFS/OPC, no S/P, 0.21 w/s ratio by weight, 60°C cure
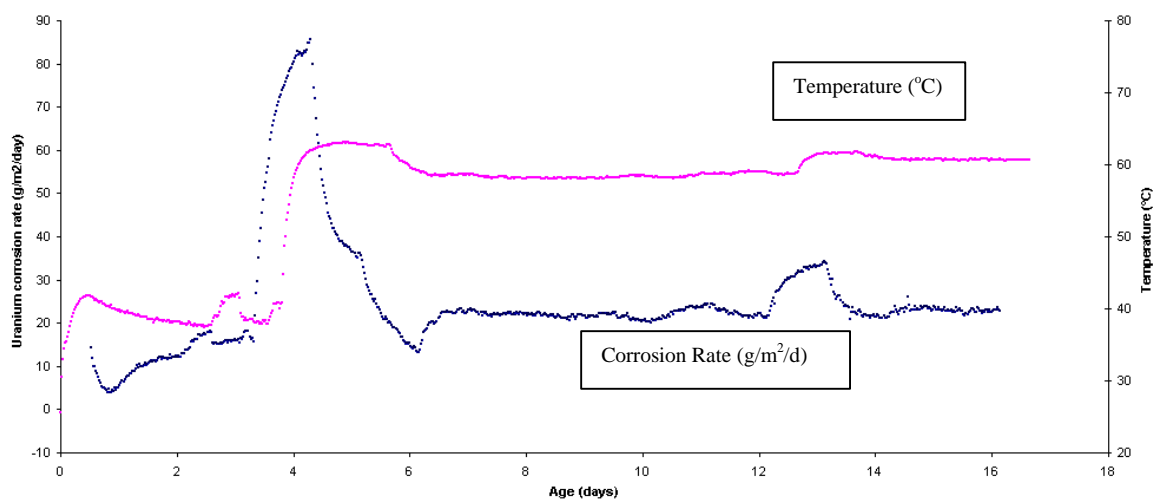
Figure 24 Log corrosion rate against temperature
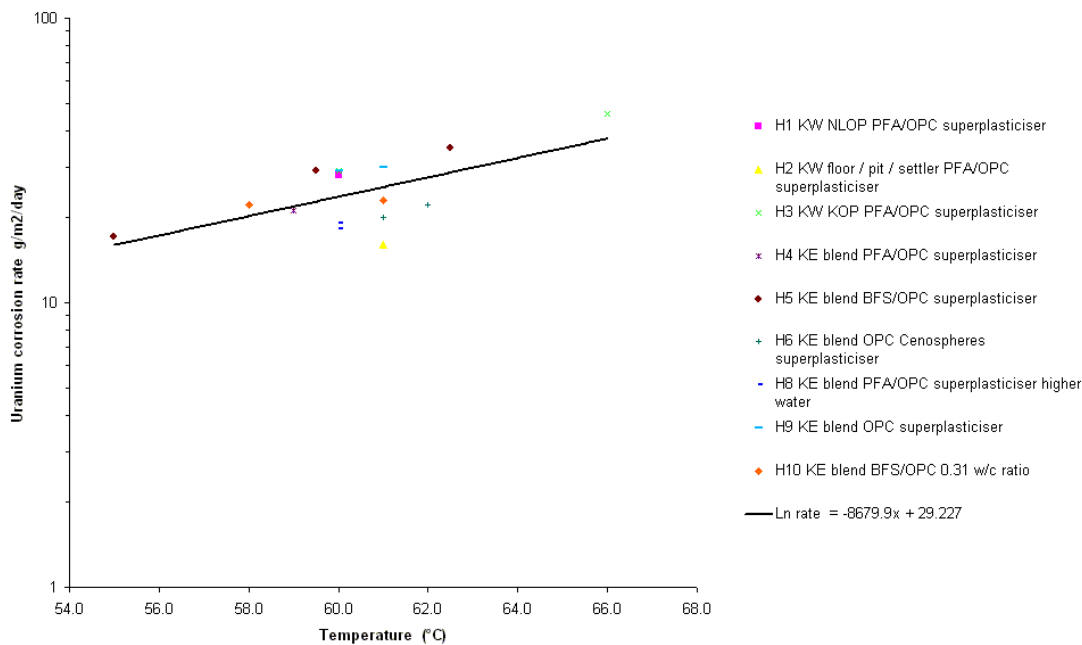
Figure 25 Log corrosion rate against inverse temperature
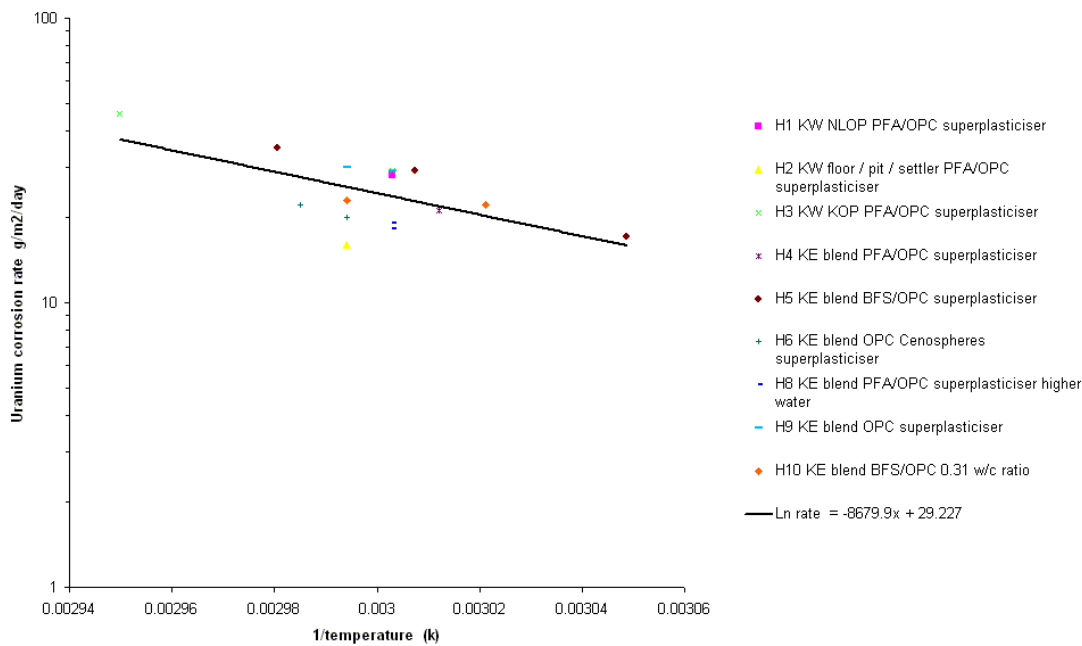
**Figure 26 Normalised corrosion rate against w/c[*] ratio by weight**
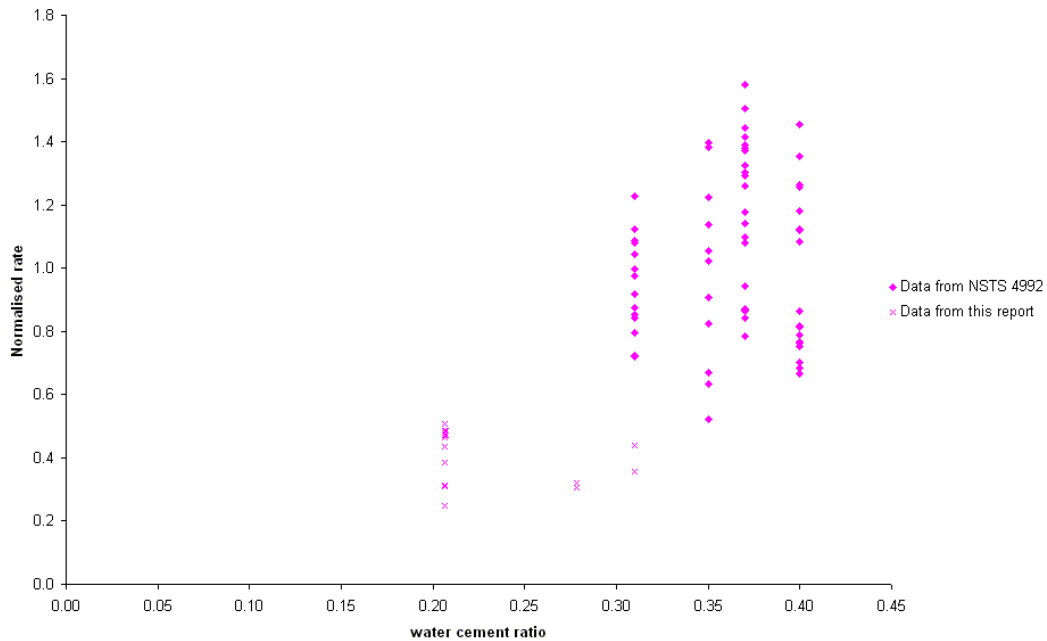
Figure 27 Normalised corrosion rate against w/s [**] ratio by weight

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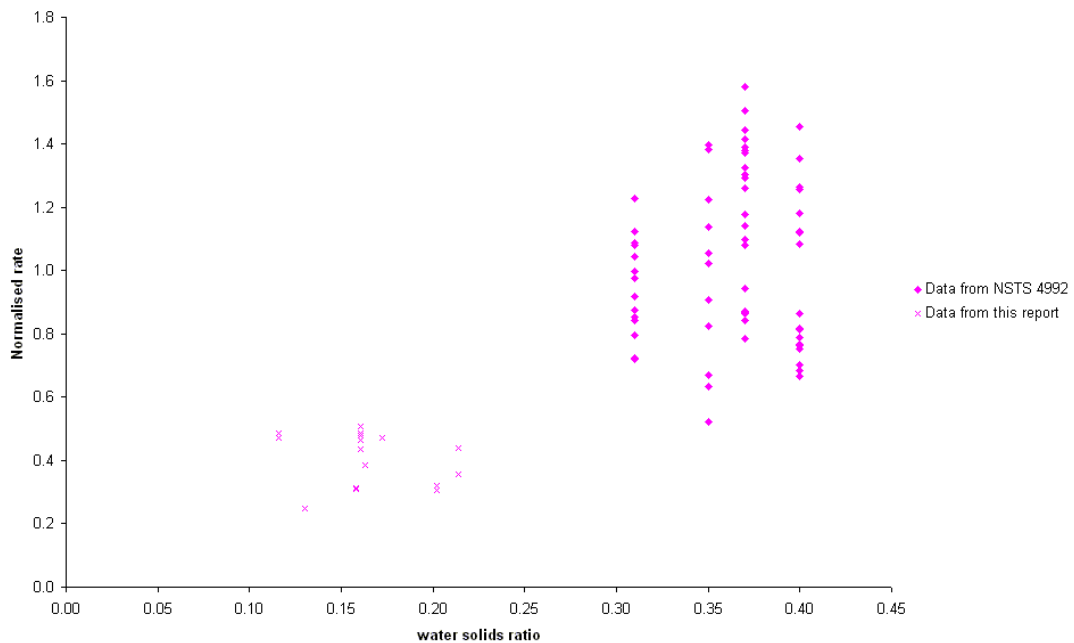
[*] w/c = weight of water divided by weight of cement - i.e. BFS, OPC or PFA
[**] w/s is the weight of water divided by the total weight of solids (i.e. simulant plus BFS, OPC or PFA and additives)

Figure 28 Normalised corrosion rate against % solids[*] content by weight
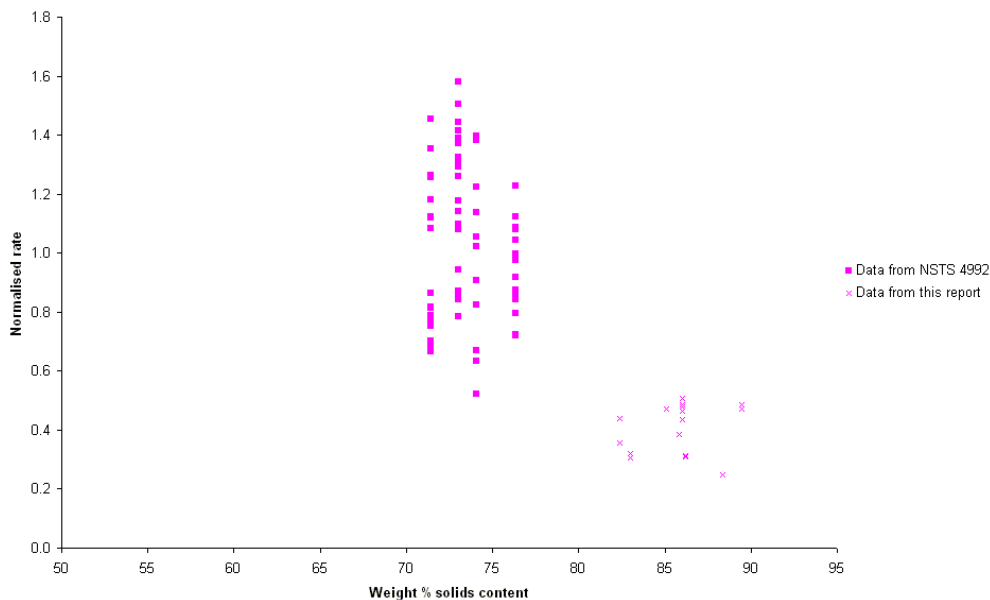
Figure 29 Normalised corrosion rate against % solids[**] content by volume

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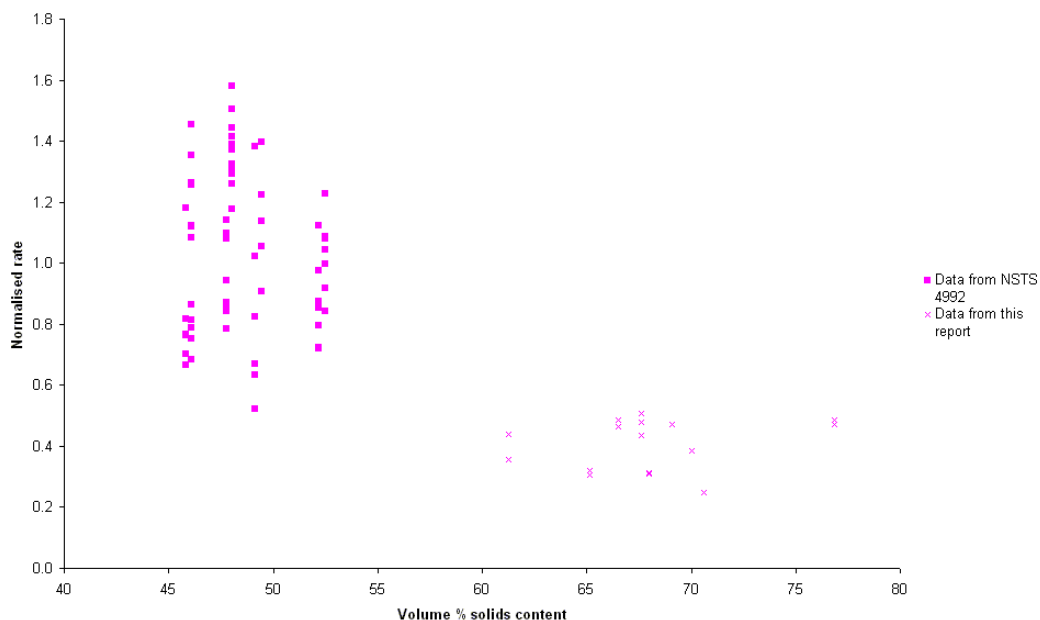
[*] % solids is the weight of solids (i.e. simulant plus BFS, OPC or PFA and additives) divided by the total weight of solids (i.e. simulant plus BFS, OPC or PFA and additives) and water
[**] % solids is the volume of solids (i.e. simulant plus BFS, OPC or PFA and additives) divided by the total volume of solids (i.e. simulant plus BFS, OPC or PFA and additives) and water

Figure 30 comparison of corrosion rates with those generated in NSTS (04) 4992
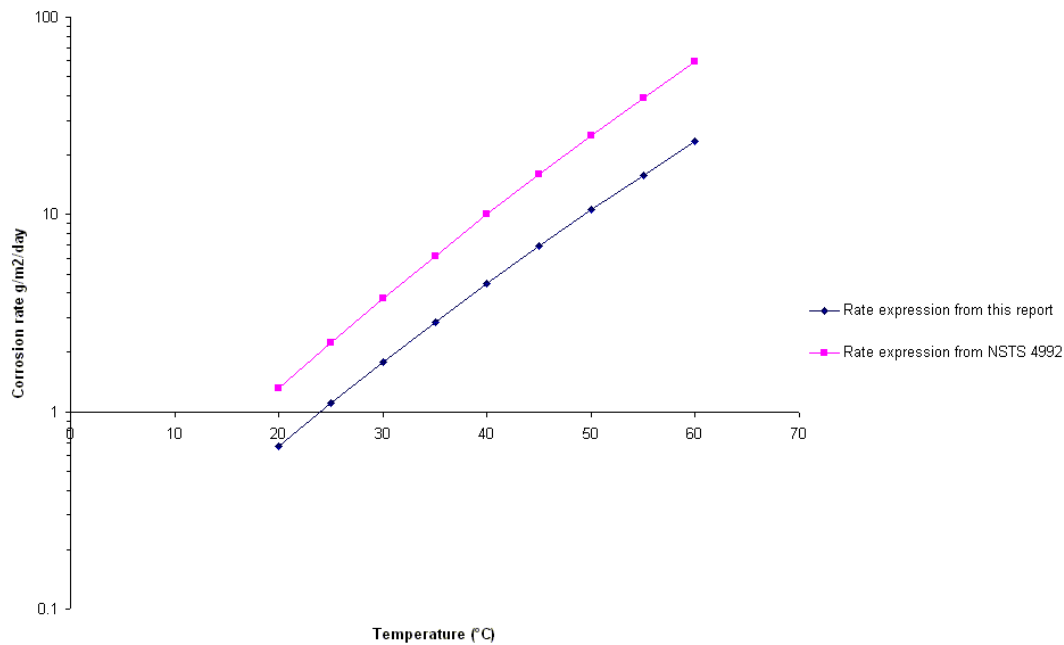
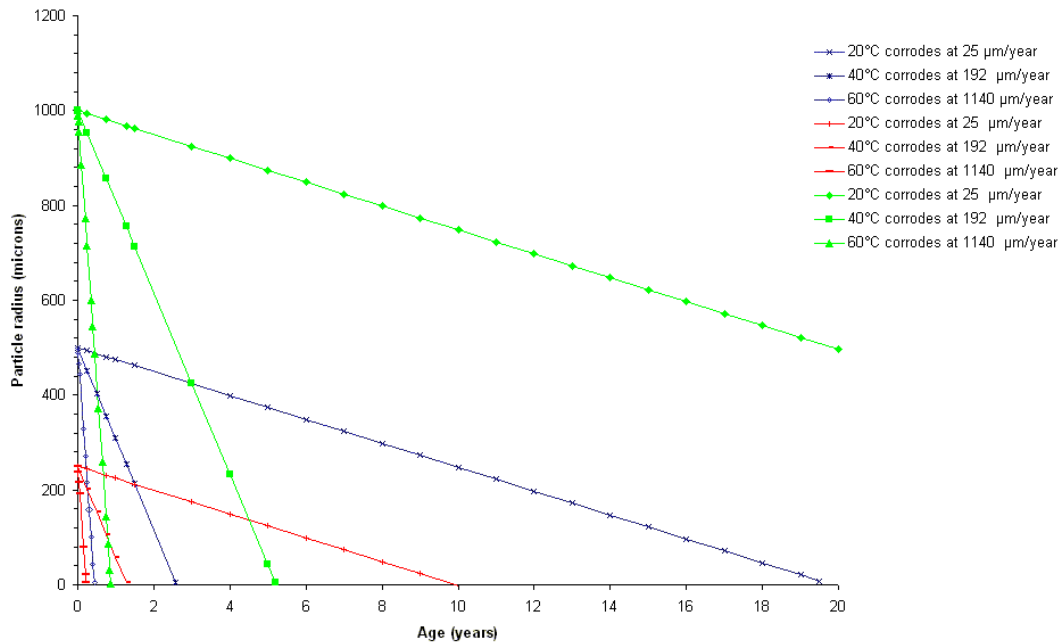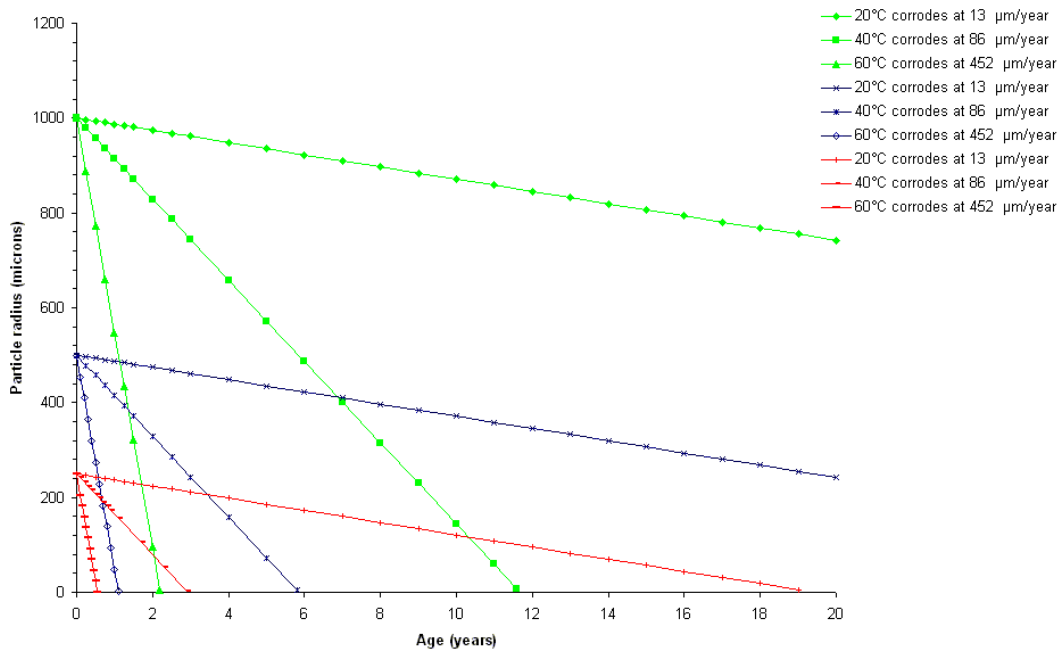**Figure 31 Size of uranium particle with time and temperature using rate expression from NSTS (04) 4992**

Figure 32 Size of uranium particle with time and temperature using minimised rate expression from this report

9. DISTRIBUTION

Name	Location
Encapsulation team	B170 Sellafield
BNFL Inc	Richland
Fluor Hanford	Richland
Information Retrieval Services	IRS, Risley